

Rhombohedral to cubic phase transition in the relaxor ferroelectric PZN

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 L233

(<http://iopscience.iop.org/0953-8984/18/19/L02>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 10:38

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Rhombohedral to cubic phase transition in the relaxor ferroelectric PZN

J S Forrester¹, E H Kisi¹, K S Knight² and C J Howard³¹ School of Engineering, The University of Newcastle, NSW 2308, Australia² ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK³ Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, AustraliaE-mail: jenny.forrester@newcastle.edu.au, Erich.Kisi@newcastle.edu.au, K.S.Knight@rl.ac.uk and cjh@ansto.gov.au

Received 20 March 2006, in final form 5 April 2006

Published 25 April 2006

Online at stacks.iop.org/JPhysCM/18/L233**Abstract**

The structure and phase transition in lead zinc niobate (PZN) were studied using very high resolution powder neutron diffraction between 4.2 and 450 K. The structure is unequivocally rhombohedral in space group $R3m$ with $a = 4.06048 \text{ \AA}$ and $\alpha = 89.8693^\circ$ at 4.2 K. No low symmetry phases were observed, nor was an octahedral tilting transition to $R3c$ as occurs in some parallel systems (e.g. PZT). Within the rhombohedral structure, large average ion displacements were found relative to the rather small spontaneous strains. On heating, a transition to a cubic perovskite occurs, with a critical temperature of $\sim 384 \text{ K}$.

1. Introduction

There has been considerable technological interest in relaxor ferroelectric materials in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN–PT) system due to their excellent piezoelectric properties [1, 2]. PZN–PT single crystals show the largest piezoelectric coefficient ($d_{33} \sim 2500 \text{ pC N}^{-1}$) and piezoelectric strains (up to 1.7%) of any practical piezoelectric material [3]. In common with many ferroelectrics, PZN–PT materials have distorted perovskite structures, in this case with multiple occupancy of the B cation site. In addition to their exceptional properties the materials are intriguing, because unlike other ferroelectric materials the maximum piezoelectric response and the spontaneous polarization are not collinear. The large electromechanical coupling and piezoelectric strain occurs in the [001] direction (referred to the parent cubic phase), whereas the spontaneous polarization is directed along [111] in the notionally rhombohedral crystals. Theories for the observed behaviour of these materials include the following:

- (i) large elastic compliance s_{33} [1, 4], which allows greater mechanical deformation along the principal axes per unit of applied electric field;

- (ii) polarization rotation under applied field [5];
- (iii) electric field induced phase transitions from rhombohedral to tetragonal [2, 6, 7], monoclinic [8, 9] or orthorhombic symmetry [10, 11].

The last explanation has been prominent in the literature and has undergone many revisions. The neutron diffraction results of Forrester *et al* [12] and group theoretical arguments of Kisi *et al* [4] do not support the diverse range of phases and structures reported within this system⁴.

Much of the work has relied upon structures inferred from x-ray scans over relatively few (sometimes only one) reflection(s) from poly-domain single crystals either under electric field or after poling [2, 6–13]. These observations concerning the structure and phase transitions in PZN–PT offer surprisingly little insight into the large piezoelectric response of PZN–PT as they are based on the lattice symmetry alone. The magnitude of the large piezoelectric response depends on the relative positions of the ions (spontaneous polarization) and their relative motion under external stimuli (applied stress or electric field—the induced polarization), none of which have been explored in detail. The rhombohedral structure ($R3m$) of the as-grown crystals was recently confirmed [14] and the ground state (zero field, zero stress) ion positions determined for the first time at 4.2 and 295 K using neutron powder diffraction [15]. Further studies are required to establish these parameters from samples spanning the entire temperature–composition phase diagram of which this work forms a part.

The controversy over the structure of PZN–PT crystals is due to several factors: (i) the crystals contain microscopic ferroelectric domains, (ii) the material has a very large elastic compliance—nearly an order of magnitude larger than PZT, which makes the crystals susceptible to elastic macro and micro strains, and (iii) the unit cell parameters are closely pseudo-cubic. The pseudo-symmetry worsens as the morphotropic boundary is approached, leading to the greatest uncertainty at the very point where the physical properties are optimal. The end-member PZN has excellent piezoelectric properties in its own right (approximately half those of PZN–8%PT and superior to the industry standard—PZT). It has the simplest *B*-site occupancy and is compositionally remote from any complications (structural distortions, phase coexistence etc) associated with the morphotropic boundary. It therefore provides the ideal starting point for a re-investigation of the phase transitions in the PZN–PT system.

This paper reports the results of a very high resolution neutron powder diffraction study of the phase transition and spontaneous polarization in PZN over the temperature range 4.2–430 K. The spontaneous polarization and spontaneous strains are observed to have a different temperature response, suggesting different transition orders.

2. Experimental details

Neutron powder diffraction patterns were recorded on the HRPD diffractometer at the ISIS facility, Rutherford Appleton Laboratory, UK. The instrument has a resolution of $\Delta d/d = 4 \times 10^{-4}$ in the absence of sample induced broadening. A strength of the neutron technique is that the scattering length of oxygen is comparable to that of the metal ions, giving far greater confidence in the determined ion positions. Additionally, neutrons are only lightly absorbed by this material, making the results free from surface relaxation effects [14].

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ single crystals in the size range 0.5–15 mm were produced by the flux-growth method [16]. Crystals were extracted from the flux in a hot HNO_3 solution and lightly crushed in an agate mortar and pestle. The powder chosen was able to pass through a coarse sieve (143 μm), a compromise to ensure good powder averaging in the $\sim 2 \text{ cm}^3$

⁴ Although PZT is a conventional rather than a relaxor ferroelectric.

Table 1. Crystal structure of PZN at 4.2 K [15].

	<i>x</i>	<i>y</i>	<i>z</i>
<i>T</i> (K)	4.2		
Pb	1/2	1/2	1/2
Nb	0.0258(3)	0.0258(3)	0.0258(3)
Zn ^a	0.0258(3)	0.0258(3)	0.0258(3)
O	0.5438(5)	0.0547(4)	0.0547(4)
<i>a</i> (Å)	4.06048(6)		
α (deg)	89.8693(4)		
<i>S</i> ₄₀₀ (Å ⁻⁴)	9.5 × 10 ⁻⁹		

^a Constrained to be the same as Nb.

sample without causing particle size broadening or lattice strains. The sample was held in a thin walled aluminium can within a liquid helium cryostat. Diffraction patterns were recorded from 30 000 to 130 000 μ s whilst pausing at constant temperature for 20 min, including 2 min for temperature equilibration. Patterns of approximately 1.5 h duration were recorded at 300 K before cooling, 4.2 K and 300 K at the end of the temperature cycle.

Rietveld analyses were conducted using GSAS [17]. Data from both the high resolution backscattering bank and the high intensity 90° detector bank were used simultaneously in crystal structure refinements from which ion positions were extracted. A second refinement series was conducted using only data from the backscattering bank to provide refined lattice parameters with slightly improved precision. The refined lattice parameters differ only in the degree of scatter about the mean trend. Refinements typically included lattice parameters, atom coordinates, isotropic thermal parameters (Pb, Zn/Nb), anisotropic thermal parameters (O), scale, eight polynomial background parameters, two peak profile parameters and one diffractometer constant (DIF A). The anisotropic peak broadening model of Stephens [18] was necessary to compensate for the slightly broadened *h*00 reflections. The same starting model, based upon the 4.2 K best fit, was used as the starting point for refinements at all temperatures.

3. Results and discussion

None of the new phases reported in the PZN–PT or PZT systems were observed in this work. Neither was any evidence found for the two-phase co-existence reported by Lebon *et al* [13]. The crystal structure of PZN at 4.2 K was recently confirmed to be rhombohedral in *R3m* from high resolution neutron powder diffraction [15]. It is reproduced in table 1. Within the rhombohedral structure, large average ion displacements were found relative to the rather small spontaneous strains.

The temperature evolution of the lattice parameters is illustrated in figures 1 and 2. The rhombohedral distortion ($90^\circ - \alpha$) indicates a rhombohedral (R) \rightarrow cubic (C) transition at approximately 384 K, some ~ 35 K below the transition temperature shown on the conventional phase diagram [1]. A similar observation was made during neutron diffraction studies of a 4.5%PT single crystal [12]. Apart from this difference, the transition appears continuous and is allowed to be so under Landau theory [12, 19]. The solid line in figure 1 illustrates that the data fit very well to an equation of the form

$$90^\circ - \alpha = C[T_S(\coth(T_S/T_C) - \coth(T_S/T))]^{\frac{1}{2}} \quad (1)$$

with the constant $C = 0.00843$, the critical temperature $T_C = 384$ K and the saturation temperature $T_S = 177$ K. We may explore the transition in more detail with the assistance

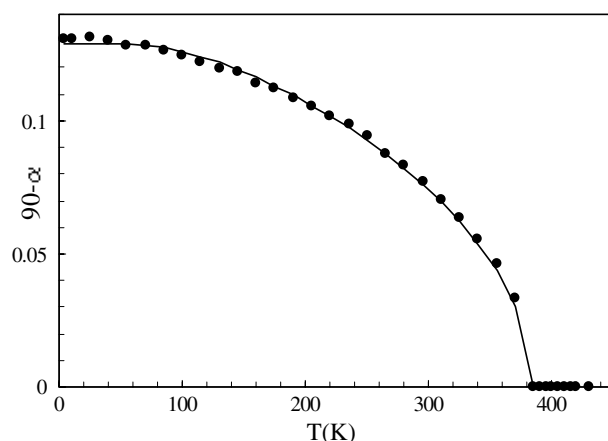


Figure 1. Rhombohedral angle ($90^\circ - \alpha$) as a measure of spontaneous strain between 4.2 and 430 K showing the transition to cubic at 384 K. The fitted line is to a tricritical Landau model with a refined saturation temperature of 177 K.

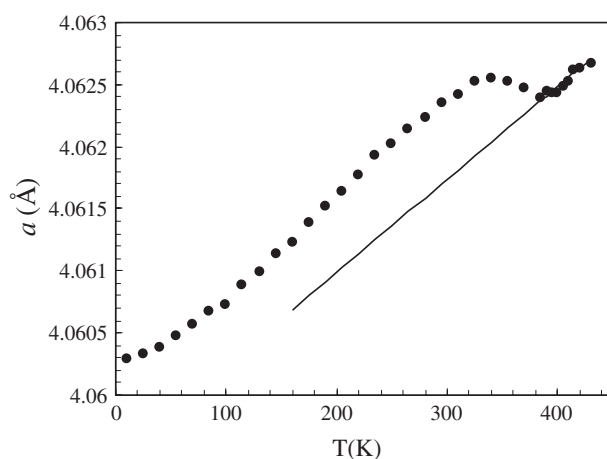


Figure 2. Lattice parameter a , as a function of temperature. The solid line is the extrapolation of the cubic lattice parameter to lower temperature. The volume expansion on cooling is approximated by the difference between the solid line and the points although the extrapolation is not rigorous.

of the computer program ISOTROPY [20]. For this transition, the appropriate irreducible representation for the order parameter is Γ_4^- . The irreducible representation for the spontaneous shear strains is Γ_5^+ . In the thermodynamic view of perovskite phase transitions [21], if these representations differ, then the spontaneous strain is proportional to the square of the order parameter. The close fit of the spontaneous strains to (1) with exponent 1/2 implies that the temperature dependence of the order parameter has exponent 1/4, consistent with a tri-critical transition.

The lattice parameter a is plotted against temperature in figure 2. Due to the small departure from $\alpha = 90^\circ$, the cell volume mirrors this behaviour closely and is not shown. Several features are observable in the figure. At ~ 325 K there is a region ~ 60 K in width, immediately before the phase transition, during which the lattice contracts. A similar observation of negative thermal expansion in PZN was made by Lebon *et al* [13], although the

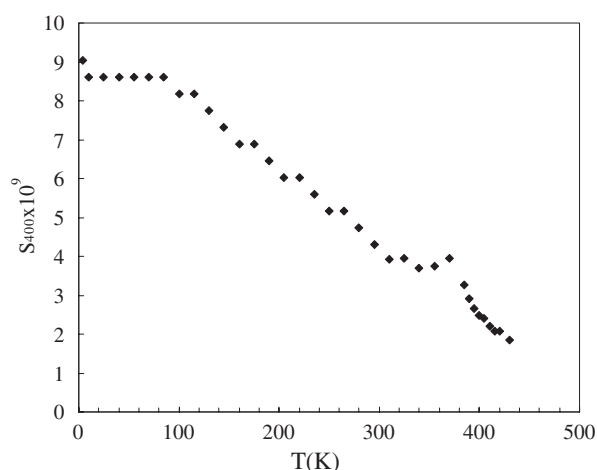


Figure 3. Anisotropic broadening parameter S_{400} (\AA^{-4}) determined during the Rietveld refinements.

lower precision of those results showed no curvature in this region. In that work, the negative expansion was interpreted as evidence for two-phase R + C co-existence, which was not observed here. Other ferroelectric phases such as BaTiO_3 show similar effects when examined closely (e.g. figure 2 of [22]). Negative thermal expansion is generally associated with the rotation of rigid structural units. In this case, however, octahedral rotation has been ruled out by previous structural analysis [15]. Instead, it appears to be a volume dilation on cooling due to the symmetry change from cubic to rhombohedral. This may be understood geometrically as the imposition of a ferroelectric distortion onto a structure in which the B cation to oxygen bond is strongly compressed ($\sim 2\%$), which must lead, *ceteris paribus*, to less efficient packing and a volume dilation. It is apparent that the rate of expansion of the rhombohedral phase in the range 220–325 K is the same as in the cubic phase above 385 K. Below this, in the temperature region from 100 to 220 K is a further linear region with an increased slope. The implication is that below 220 K the volume difference between the parent cubic phase and the rhombohedral phase is less. This may be associated with a greater degree of order within the polar nano-regions thought to be responsible for relaxor behaviour or within the microscopic ferroelectric domain structure.

Throughout the temperature range of the R phase (≤ 384 K) a small amount of anisotropic peak broadening was observed. The systematics are such that the $h00$ peaks were broadest. For rhombohedral symmetry in space group $R3m$, the model of Stephens [18] allows four anisotropic broadening parameters: S_{400} , S_{220} , S_{310} and S_{211} . Trial refinements indicated that S_{400} was the largest and the others so small they could be set to zero without compromising the fit. A plot of S_{400} as a function of temperature is shown in figure 3. The figure shows a saturated region below 100 K. Above 100 K is a linear decrease with increasing temperature, most likely due to inter-domain strains which decrease as the spontaneous strains decrease. A small rise in the value of S_{400} occurs on both sides of the transition. Similar observations have been made in ferroelastic As_2O_5 [23] and more recently in the perovskite PrAlO_3 [24], where the peak breadths at temperatures immediately adjacent to the transitions were 2–2.5 times greater than those more remote from the transition. The effect observed here is much smaller (figure 3). In As_2O_5 and PrAlO_3 , the peaks broadened were those which were split during the transition. In PZN, the R \rightarrow C transition does not split the $h00$ peaks and so the analogy is

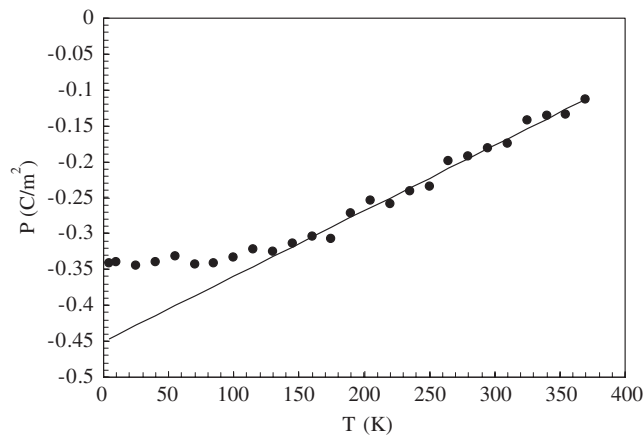


Figure 4. Spontaneous polarization (P) estimated from refined ion positions in PZN and the formal valencies.

imperfect. The PZN–PT phase diagram [1, 12] shows a tetragonal (T) phase intermediate to the cubic and rhombohedral phases in the range 5–11% PT. The tetragonal region on the phase diagram is only ~ 25 K wide at 5% PT and it is not drawn below this composition; however, the expectation is that the $R \rightarrow T$ phase boundary and the $T \rightarrow C$ phase boundary converge to a single $R \rightarrow C$ boundary at 0% PT. This agrees with our diffraction patterns and the analysis above. However, a transition to tetragonal *would* split the $h00$ peaks and is therefore consistent with additional peak broadening at the transition, as observed in figure 3. The tetragonal phase is known to persist in two-phase R+T and T+C mixtures to 4.5% PT [25], just below its formal extent on the phase diagram, but a single phase tetragonal region greater than 5 K in extent was not observed at this composition. Our interpretation of the additional peak broadening at the $R \rightarrow C$ transition is that it is the result of tetragonal fluctuations not sufficiently ordered to produce a recognizable tetragonal diffraction pattern. If a tetragonal region exists in PZN, it and its associated two-phase regions are less than 5 K in extent.

Another way to examine the transition, and a critical one for a polar material, is to consider the spontaneous polarization. The ion positions refined during Rietveld analysis allowed the spontaneous polarization to be estimated as a function of temperature. Taking the threefold axis of the rhombohedral structure as the principal direction, the distance, d , of each atom from the (arbitrary in $R3m$) origin plane is given by

$$d = a(xi + yj + zk) \cdot (i + j + k) / \sqrt{3} \quad (2)$$

where x, y, z are the ion coordinates within the unit cell and i, j, k are unit vectors along the unit cell edges. For simplicity, we have approximated the rhombohedral angle as 90° . The spontaneous polarization is then given by

$$P = \sum Zd \quad (3)$$

where Z is the charge (or valence) of each ion and the sum is over all ions within one unit cell. The major uncertainty in the computed polarizations is in the value of Z for the ions. Darlington *et al* [22] have shown that, for BaTiO_3 , the agreement of computed polarizations with the macroscopic polarization is sometimes better using the apparent charges and sometimes using the formal valencies. Despite the uncertainty, results were consistent over the temperature stability range of individual phases. Figure 4 illustrates the computed values based upon the

formal valencies for convenience. The polarization appears to have saturated at approximately -0.35 C m^{-2} below 130 K. This value is slightly larger than for BaTiO_3 [22], which has comparable spontaneous strains.

Above 130 K the polarization varies linearly with temperature. The polarization, however, does not fall to zero at the transition temperature (384 K) but retains a remanent value estimated at -0.11 C m^{-2} . The extrapolated transition temperature from the polarization is $\sim 490 \text{ K}$, quite different from that at which the spontaneous strains fall to zero. This casts some doubt over the order of the transition. The spontaneous strains suggest a tri-critical transition; however, the existence of a substantial polarization at the transition temperature requires that the transition is first order. We conclude from this that the transition is most likely weakly first order.

4. Conclusions

This paper has demonstrated that the average crystal structure of PZN, the end-member of the PZN–PT phase diagram, is undoubtedly rhombohedral in $R3m$. Neutrons are far more penetrating than even the 67 keV x-rays used in some of the synchrotron studies and so we are confident that this result represents the bulk material structure. The material is free from the low-temperature phase transitions and the two-phase coexistence reported in PZT, which until recently had a very similar phase diagram.

According to the lattice parameters (spontaneous strains), PZN undergoes a tri-critical transition to the cubic phase at 384 K, some 35 K lower than shown in the conventional phase diagram [1]. The ion positions (spontaneous polarization) however indicate a first-order transition, with the polarization retaining approximately one-third of its low temperature value right up to the transition temperature.

The work has been supported by the Australian Research Council, the Australian Institute of Nuclear Science and Engineering and the Access to Major Research Facilities Program.

References

- [1] Kuwata J, Uchino K and Nomura S 1981 *Ferroelectrics* **37** 579–82
- [2] Park S-E and Shrout T R 1997 *J. Appl. Phys.* **82** 1804–11
- [3] Ogawa T, Yamauchi Y, Numamoto Y, Matsushita M and Tachi Y 2002 *Japan. J. Appl. Phys.* **41** L55–7
- [4] Kisi E H, Piltz R O, Forrester J S and Howard C J 2003 *J. Phys.: Condens. Matter* **15** 3631–40
- [5] Fu H and Cohen R E 2000 *Nature* **403** 281–3
- [6] Paik D-S, Park S-E, Wada S, Liu S-F and Shrout T R 1999 *J. Appl. Phys.* **85** 1080–3
- [7] Durbin M K, Jacobs E W, Hicks J C and Park S-E 1999 *Appl. Phys. Lett.* **74** 2848–50
- [8] Noheda B, Cox D E, Shirane G, Park S-E, Cross L E and Zhong Z 2001 *Phys. Rev. Lett.* **86** 3891–4
- [9] Noheda B, Zhong Z, Cox D E, Shirane G, Park S-E and Rehring P 2002 *Phys. Rev. B* **65** 224101
- [10] Cox D E, Noheda B, Shirane G, Uesu Y, Fujishiro K and Yamada Y 2001 *Appl. Phys. Lett.* **79** 400–2
- [11] La-Orauttapong D, Noheda B, Ye Z-G, Gehring P M, Toulouse J, Cox D E and Shirane G 2002 *Phys. Rev. B* **65** 144101
- [12] Forrester J S, Piltz R O, Kisi E H and McIntyre G J 2001 *J. Phys.: Condens. Matter* **13** L825–33
- [13] Lebon A, Dammak H, Calvarin G and Ould Ahmedou I 2002 *J. Phys.: Condens. Matter* **14** 7035–43
- [14] Kisi E H and Forrester J S 2005 *J. Phys.: Condens. Matter* **17** L381–4
- [15] Kisi E H, Forrester J S and Knight K S 2006 *Acta Crystallogr. C* **60** at press
- [16] Mulvihill M L, Park S-E, Risch G, Li Z, Uchino K and Shrout T R 1996 *Japan. J. Appl. Phys.* **35** 3984–90
- [17] Larson A C and Von Dreele R B 2004 *General Structure Analysis System (GSAS)* Los Alamos National Laboratory Report LAUR 86-748
- [18] Stephens P 1999 *J. Appl. Crystallogr.* **32** 281–9
- [19] Stokes H T, Kisi E H, Hatch D M and Howard C J 2002 *Acta Crystallogr. B* **58** 934–8
- [20] Stokes H T and Hatch D M 2002 www.physics.byu.edu/~stokesh/isotropy.html

- [21] Carpenter M A, Salje E K H and Graeme-Barber A 1998 *Eur. J. Mineral.* **10** 621–91
- [22] Darlington C N W, David W I F and Knight K S 1994 *Phase Transit.* **48** 217–36
- [23] Redfern S A T and Salje E 1988 *J. Phys. C: Solid State Phys.* **21** 277–85
- [24] Carpenter M A, Howard C J, Kennedy B and Knight K S 2005 *Phys. Rev. B* **72** 024118
- [25] Forrester J S, Kisi E H and Knight K S 2005 *Physica B* at press